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THERMAL STUDIES ON THE ADDUCTS OF BIS(1-(2-THENOYL)-3,3,3-TRIFLUOROACETONATE) OXOVANADIUM(IV)

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ABSTRACT

A series of VO(tta)$_2$ adducts were previously prepared and characterized. The study of these adducts using DTA and TG techniques allowed us to determine the degree of thermal stability of these compounds and to observe the loss of one mole of coordinated base in the first endothermic process.

By means of the study of the first process through the DSC technique, the activation energy and enthalpy were calculated, establishing relationships between basic character and the bonding force with the vanadium atom in the adducts formed. Moreover, good relationships have been established between the values obtained from infrared spectroscopy for the vibration ν(V=O) and the activation energy values.

INTRODUCTION

We have previously reported [1–3] a thermal study of a series of bis(β-diketonate) oxovanadium(IV) adducts, where the β-diketones employed are: 1,3-diphenylpropane-dione [1–3], 1-phenyl-1,3-butanedione and 2,4-pentane-dione, establishing a relationship between the base bonding-force with the vanadium atom and the values obtained for the activation energy, basic character, thermal stability, infrared spectroscopy for the vibration ν(V=O) and functional groups of the β-diketone or pyridine utilised.

In the present work we report a study of the process of thermal decomposition of VO(tta)$_2$ adducts, where the 1-(2-thenoyl)-3,3,3-trifluoroacetone ($C_4H_3SCOCH_2COCF_3$) (tta), is a halogen β-diketone. These compounds were previously synthesized by us [4] and the study was carried out using spectroscopic and magnetic susceptibility techniques to which we assign the general formula VO(tta)$_2 \cdot$ B (B = pyridine (Py), 3-methylpyridine (3-MP), 4-methylpyridine (4-MP), 3,5-dimethylpyridine (3,5-DMP), 3-aminepyridine (3-AP) and 4-aminepyridine (4-AP)).

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The study of these adducts using DTA and TG techniques allowed the degree of thermal stability of these compounds to be determined, and to observe the loss of one molecule of coordinated base in the first endothermic process.

By means of the study of the first process through the DSC technique, the activation energy and the enthalpy were calculated, establishing relationships between pK_b values and bonding force with the vanadium atom in the adducts formed.

Moreover, relationships have been established among the values obtained from infrared spectroscopy for the vibration $\nu(V{=}O)$ and the activation energy values.

All adducts obtained with tta present greater values of E_a and initial temperature for the process of loss of base than obtained with other β-diketones.

EXPERIMENTAL

Preparation of compounds

The bis(1-(2-thenoyl)-3,3,3-trifluoroacetonate) oxovanadium(IV) complex and its adducts with pyridine and substituted pyridines were prepared following a method described earlier [4].

Materials

Vanadium(IV)-oxi-sulphate, 1-(2-thenoyl)-3,3,3-trifluoroacetone, pyridine and substituted pyridines were obtained commercially (Merck and Fluka) and used without further purification.

Analytical method

Elemental analyses were performed with a Perkin-Elmer model 240-B. Vanadium was determined by atomic absorption with a Perkin-Elmer (model 430) atomic absorption spectrophotometer after decomposing the compounds with a concentrated HNO_3/H_2SO_4 mixture (1 : 1).

The analytical data for the compounds are given in Table 1.

Differential thermal analysis and thermogravimetric analysis

Thermal measurements were performed using a Mettler HE-20 thermobalance, with DTA accessory fitted. The analytical constants were: DTA range, 20 mV, 33 mcal s^{-1}; heating rate, 5°C min^{-1}; TG range, 20 mV; record rate, 20 cm h^{-1}; reference, Al_2O_3; sample mass, 20 mg; thermocouple, Pt/Pt–Rh.

TABLE 1

Analytical data

Compound	% Calculated				% Found			
	C	H	N	V	C	H	N	V
VO(tta)$_2$	37.54	1.56	–	9.96	37.21	1.55	–	9.97
VO(tta)$_2$·Py	42.68	2.20	2.37	8.62	42.51	2.15	2.20	8.44
VO(tta)$_2$·3-MP	43.67	2.48	2.31	8.42	43.37	2.23	2.27	8.25
VO(tta)$_2$·4-MP	43.67	2.48	2.31	8.42	43.45	2.35	2.29	8.30
VO(tta)$_2$·3,5-DMP	44.62	2.74	2.26	8.23	44.55	2.81	2.24	8.32
VO(tta)$_2$·3-AP	31.71	2.47	4.62	8.41	31.68	2.48	4.63	8.35
VO(tta)$_2$·4-AP	31.71	2.47	4.62	8.41	31.63	2.43	4.55	8.60

TABLE 2

Thermal data for the decomposition of VO(tta)$_2$·B

Compound	Temperature (°C)	$\Delta m/m$ (%)		Process	Identified compound
		calc	exp		
VO(tta)$_2$	250–430	82.20	80.10	Exothermic	V_2O_5
VO(tta)$_2$·Py	116–168	13.40	13.30	Endothermic	$VO(C_8H_4F_3O_2S)$
	240–430	82.20	82.30	Exothermic	V_2O_5
VO(tta)$_2$·3-MP	126–180	15.40	15.80	Endothermic	$VO(C_8H_4F_3O_2S)$
	220–490	82.20	82.45	Exothermic	V_2O_5
VO(tta)$_2$·4-MP	120–145	15.40	15.30	Endothermic	$VO(C_8H_4F_3O_2S)$
	220–452	82.20	82.35	Exothermic	V_2O_5
VO(tta)$_2$·3,5-DMP	160–205	17.32	17.50	Endothermic	$VO(C_8H_4F_3O_2S)$
	254–458	82.20	82.50	Exothermic	V_2O_5
VO(tta)$_2$·3-AP	167–185	15.54	15.70	Endothermic	$VO(C_8H_4F_3O_2S)$
	255–485	82.20	82.10	Exothermic	V_2O_5
VO(tta)$_2$·4-AP	206–224	15.54	15.60	Endothermic	$VO(C_8H_4F_3O_2S)$
	256–490	82.20	82.37	Exothermic	V_2O_5

The instrument was calibrated employing indium as standard substance. The analyses were carried out in a dynamic nitrogen atmosphere to 300°C and then in an oxygen atmosphere to 600°C.

Data for the temperatures of thermal transitions and mass loss determination are shown in Table 2.

Differential scanning calorimetry

Thermal measurements were made using a Mettler TA 3000 system with a Mettler differential scanning calorimeter (DSC 20). Samples of ~ 5 mg were used so as to render the degree of temperature non-uniformity within the sample insignificant. An aluminium pan was used under a dry nitrogen atmosphere. The scanning rate used was 2°C min^{-1}, and the instrument

TABLE 3

Infrared and kinetic data for $VO(tta)_2 \cdot B$

Compound	ν(V=O) (cm^{-1})	Temperature (°C) [a] T_i	T_p	T_f	ΔH (kcal mol^{-1})	E_a (kcal mol^{-1}) [b]	pK_b
$VO(tta)_2$	910	–	–	–	–	–	–
$VO(tta)_2 \cdot Py$	972	118	152.9	168	18.5	30.85	8.87
$VO(tta)_2 \cdot$3-MP	975	126	158.9	177	16.8	25.08	8.32
$VO(tta)_2 \cdot$4-MP	968	120	137.3	145	7.5	68.86	7.98
$VO(tta)_2 \cdot$3,5-DMP	972	160	201.5	205.5	16.5	37.11	7.85
$VO(tta)_2 \cdot$3-AP	962	167	177	185	9.1	148.61	7.49
$VO(tta)_2 \cdot$4-AP	958	206.5	217.3	223.8	7.0	175.49	4.88

[a] T_i = initial temperature; T_p = peak temperature; T_t = end temperature.
[b] E_a = activation energy.

calibration was checked periodically with standard samples of indium. In all cases several runs were made and the results are shown in Table 3.

The activation energies were obtained using Thomas and Clarke's procedure [5,6]. A plot of log dH/dt vs. 1/T is obtained from DSC data and on the linear region we can obtain the activation energy using the equation

$$-\log K = -\log(\mathrm{d}H/\mathrm{d}t)(1/A) = +\frac{E_a}{2.303RT} - \log C \qquad (1)$$

where K = rate constant; A = total area of DSC peak.

When the decomposition proceeds in the linear region over the temperature range scanned by the calorimeter, the use of eqn. (1) to compute rate constants is justified. Moreover, the activation energy derived from the DSC plot represents the true activation energy for the interfacial reaction.

RESULTS AND DISCUSSION

The analytical data in Table 1 show that the stoichiometry of the complex obtained is 2 : 1 ligand–metal, and 1 : 1 base–complex for the adducts.

The DTA curves of all the compounds show a first endothermic peak between 116 and 224°C; the mass loss accompanying this endothermic transition corresponds, on the TG curve, to the loss of one molecule of base coordinated to vanadium. Afterwards, a series of exothermic processes is produced between 220 and 490°C, corresponding to the decomposition of the complex $VO(tta)_2$, and in all cases the residue was V_2O_5. The process may be schematized as follows.

$$VO(tta)_2 \cdot B_{(s)} \xrightarrow{\text{endo}} VO(tta)_{2(s)} + B_{(g)}$$

$$VO(tta)_{2(s)} \xrightarrow{\text{exo}} V_2O_{5(s)}$$

For every adduct, the loss of one mole of base occurs in a concrete interval of temperature, after which, once the process of decomposition has stopped, the residue can be identified by infrared spectroscopy as the complex $VO(tta)_2$. This supports the rupture of the V–N bonding and the loss of one molecule of base as can be seen on the TG curve.

In order to establish the degree of thermal stability, the initial temperature of the loss of base has been taken from ref. 7. In this way the thermal stability increases in the order: $VO(tta)_2 \cdot Py < VO(tta)_2 \cdot 3\text{-MP} > VO(tta)_2 \cdot 4\text{-MP} < VO(tta)_2 \cdot 3,5\text{-DMP} < VO(tta)_2 \cdot 3\text{-AP} < VO(tta)_2 \cdot 4\text{-AP}$. It is observed that the initiation temperature of the first endothermic process increases as the basicity of the ligand increases, except for the 3-methylpyridine adduct.

The DSC study of the first endothermic process of loss of the base has allowed the determination of the activation energy by the procedure proposed by Thomas and Clarke from the DSC curves for solid-state thermal decompositions of the type

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

The values of activation energy obtained for these compounds may be arranged in the order: $VO(tta)_2 \cdot Py > VO(tta)_2 \cdot 3\text{-MP} < VO(tta)_2 \cdot 4\text{-MP} > VO(tta)_2 \cdot 3,5\text{-DMP} < VO(tta)_2 \cdot 3\text{-AP} < VO(tta)_2 \cdot 4\text{-AP}$. This sequence agrees with the values obtained from infrared spectroscopy for the vibration $\nu(V{=}O)$ [4] (see Table 3): $VO(tta)_2 \cdot Py < VO(tta)_2 \cdot 3\text{-MP} > VO(tta)_2 \cdot 4\text{-MP} < VO(tta)_2 \cdot 3,5\text{-DMP} > VO(tta)_2 \cdot 3\text{-AP} > VO(tta)_2 \cdot 4\text{-AP}$.

If we compare the E_a values calculated for the adducts with 3-MP and 3,5-DMP with those obtained for the pyridine adduct, the former presents lower values as would be expected from their greater basic character. Also, these adducts present lower values of the frequency $\nu(V{=}O)$. The above seems to indicate that the transfer of electronic density from 3-MP and 3,5-DMP to the vanadyl ion is partly blocked as a consequence of steric impediment between its methyl groups and the substituent of tta.

The adduct with 4-MP presents higher values of E_a and $\nu(V{=}O)$ as would be expected from it greater basic character.

The adducts with aminopyridines present greater activation energy values of all compounds which, combined with the values for the $\nu(V{=}O)$ vibrations, indicates that the base–metal bonding is greater in these products. However, in these compounds the values obtained for E_a and $\nu(V{=}O)$ are not similar, as occurs in other compounds [1–3], which present similar values for the adduct with 3-AP and 4-AP. In this case the adduct with 3-AP presents lower values of E_a and $\nu(V{=}O)$, which may be due to steric impediment with the large substituent of tta.

All adducts obtained with tta present greater values of E_a and T_i for the process of loss of base than obtained with other β-diketonates. This indicates that the $-CF_3$ groups of tta increase the energy levels of the metal as a consequence of the inductive effect of the halogen atoms, because of which the base–metal bonding is more intense.

The values obtained for the enthalpy of the first endothermic process do not show a clear relationship with the basicity of the pyridines with respect to the higher or lower intensity of the metal–base bonding because another factor affects these enthalpies [8,9] which we were not able to evaluate with the numerical formula used.

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